Reactions of Vinyldisilanes with Ruthenium Carbonyl

Xiaosu Dai, Naokazu Kano, Masahiro Kako, and Yasuhiro Nakadaira*
Department of Chemistry, University of Electro-Communications, 1-5-1 Chofugaoka, Chofu, Tokyo 182-8585

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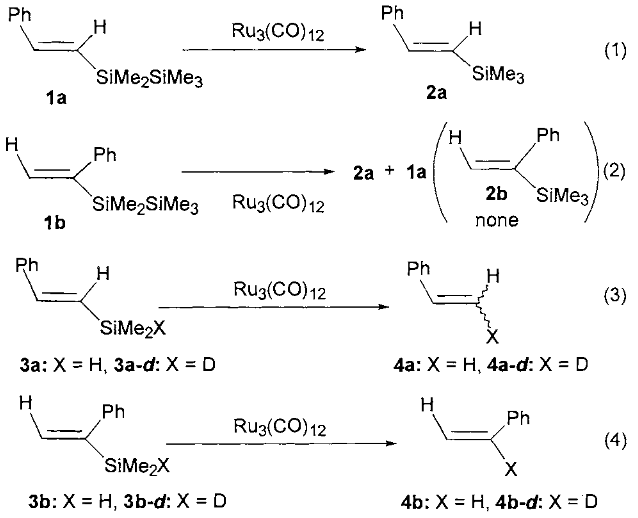
Reaction of β-styrylpentamethyldisilane (**1a**) with Ru$_3$(CO)$_{12}$ afforded β-styryltrimethylsilane (**2a**) with elimination of a dimethylsilylene unit, while under similar conditions α-isomer **1b** yielded **2a** together with **1a**. Studies on these reactions suggest the formation of silapropenyl and silylene ruthenium complexes as key intermediates.

Since the ionization energy of a Si-Si σ bond is comparable to that of a C-C π bond, vinyldisilanes are conceivable to be one of the silicon analogs of 1,3-dienes. In this sense, as 1,3-dienes readily form (diene)tricarbonylirons with an iron carbonyl complex, vinyldisilanes are expected to form (η^3-silapropenyl) (silyl) tricarbonylirons. Some years ago, we reported that vinyldisilanes react with an iron carbonyl complex to give the corresponding vinylsilane with loss of a silylene unit.[1] The unique silylene extrusion reaction has been reasonably explained by assuming the η^3-silapropenyl iron complex as a key intermediate.[2] In general, homologous transition metals form similar complexes and the corresponding heavier metal complex is expected to be more stable. Thus, in order to obtain more detailed information about the transformation of vinyldisilanes on the metal center we have examined the reaction of a homologous ruthenium carbonyl complex.

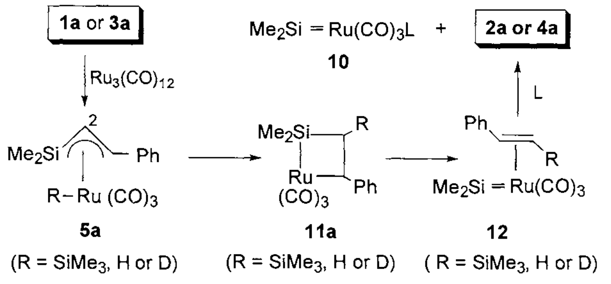
As with Fe(CO)$_5$, the reaction of β-styrylpentamethyldisilane (**1a**, 0.43 mmol) with Ru$_3$(CO)$_{12}$ (0.43 mmol) in toluene (10 ml) at 115 °C for 5 h gave β-styryltrimethylsilane (**2a**) with elimination of a dimethylsilylene unit in much higher yield, 98%[3] at 50% conversion (eq. 1). Under similar conditions, α-isomer **1b** reacted with Ru$_3$(CO)$_{12}$ to afford **2a** in 46% yield at 65% conversion but none of its α-isomer **2b** (eq. 2). Interestingly, unlike the case of Fe(CO)$_5$, the isomeric disilane **1a** was also obtained from the reaction mixture in 20% yield along with **2a** (eq. 2).[4] A dimethylsilylene unit is formally eliminated from the vinyldisilanes in both cases of **1a** and **1b**. The treatment of 1-β-styryl-1,1-diphenyltrimethyldisilane (**1c**, 0.28 mmol) with Ru$_3$(CO)$_{12}$ (0.28 mmol) in toluene (10 ml) at 115 °C for 5 h afforded **2a** in 70% yield with elimination of a diphenylsilylene unit. No scrambling of the phenyl group was observed during the extrusion reaction. This indicates that the silicon atom linked to the styryl group in **1a** should be eliminated as a silylene unit.

On the other hand, a silyl group often behaves formally as a hydride group in some reactions, such as transition metal catalyzed hydrosilylation and bis-silylation.[5] Reactions of hydrogen analogue of both **1a** and **1b**, β- and α-styryldimethylsilanes (**3a**, 0.62 mmol and **3b**, 0.62 mmol), with Ru$_3$(CO)$_{12}$ (0.62 mmol) in toluene (10 ml) at 115 °C for 5 h gave styrene in 70% and 60% yields, respectively, with concomitant loss of a dimethylsilylene unit (eqs. 3-4). In order to show clearly the fate of the hydrogen on the silicon, two kinds of deuteriosilanes **3a**-*d* and **3b**-*d* were subjected to the reaction with Ru$_3$(CO)$_{12}$ under similar conditions. The silylene extrusion proceeded regiospecifically and the products obtained were analyzed to be β-*d*- and α-*d*-styrenes **4a**, **b**-*d*, respectively, by their ^{1}H NMR spectra (eqs. 3-4). Namely, **3a**-*d* and **3b**-*d* have been converted to **4a**-*d* and **4b**-*d*, respectively.

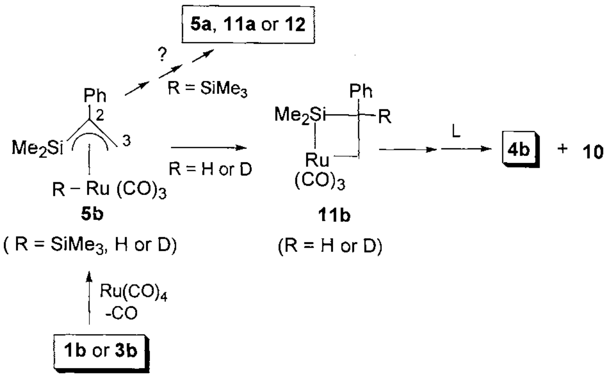


At first, to determine the organic ligand of the key intermediate η^3-silapropenyl ruthenium such as **5a** (see Scheme 1), **1a** (0.43 mmol) was heated with Ru$_3$(CO)$_{12}$ (0.43 mmol) in toluene (10 ml) containing a large excess amount of the nucleophilic trapping reagent MeOH (50 mmol) at 115 °C for 6 h to give trans-β-styryldimethylmethoxysilane (**6a**) in 75% yield together with **2a** (11%) (eq. 5). Interestingly, in the presence of a large excess amount of MeOH (Ru$_3$(CO)$_{12}$: MeOH = 1 : 114), **1b** yielded α-styryldimethylmethoxysilane (**6b**) in 95% along with trace amounts of the isomer **6a** and **2a** (eq. 6). Furthermore, in the presence of less amounts of MeOH (Ru$_3$(CO)$_{12}$: MeOH = 1 : 19) **1b** was reacted with the ruthenium carbonyl to afford **6a** in 10% yield together with **6b** and **2a** in 80% and 5% yields (eq. 6), respectively. Since the sp^2 hybridized silicon atom is extremely reactive toward nucleophiles and highly oxophilic even on the ruthenium,[6,7] the key species such as **5a** and **5b** in Schemes 1 and 2 should be trapped efficiently with MeOH to yield **6a** and **6b**, respectively. However, in the case of **1b**, formation of minor product **6a** should be noted in the presence of limited amount of MeOH. Since the trapping experiment with MeOH should afford a rutheniumsilylhydride complex such as **7** in addition to methoxysilanes **6a** and **6b** as shown in eqs. 5-6, *p*-methylstyrene (2.12 mmol) was added to the reaction mixture of **1a** (0.23 mmol) and Ru$_3$(CO)$_{12}$ (0.23 mmol) at 100 °C in toluene (10 ml) and MeOH (0.63 ml). After 10 h this caused the dehydrogenative silylation of **7** to give *p*-methylstyryltrimethylsilane (**8**) in 10% yield (eq. 7).[8]

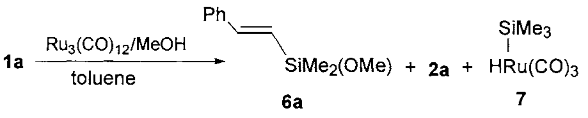
Furthermore, the treatment of **1a** (0.21 mmol) with Ru$_3$(CO)$_{12}$ (0.21 mmol) in toluene (10 ml) containing a large excess amount of diphenylacetylene (21.4 mmol) at 110 °C for 5 h afforded 1,1-dimethyltetraphenylsilole (**9**) in 8% together with **2a** in 98% (eq. 8). Under similar conditions **1b** also gave **9** in



Scheme 1.



Scheme 2.



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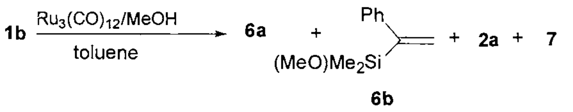

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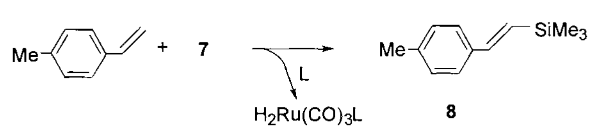

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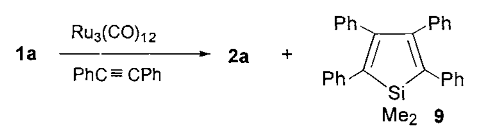

(8)

8% with **2a** and **1a** in 46 and 20% yields, respectively. The formation of **9** suggests the intervention of a silylene complex such as **10** and **12** (see Scheme 1).[10]

On the basis of several pieces of experimental evidence described, the plausible transformation mechanism of vinyldisilanes **1a** and **1b** on the ruthenium is illustrated in Schemes 1 and 2. As in the case of $Fe(CO)_5$,[1] **1a** is transformed to (η^3-silapropenyl)(trimethylsilyl)tricarbonylruthenium (**5a**) first, and then the trimethylsilyl group on the ruthenium atom migrates to the C(2) atom of the silapropenyl ligand to afford ruthenacycle **11a**.[10] Subsequent retro-cycloaddition of **11a** leads to silylene complex **12** which would release **2a** together with silylene ruthenium complex **10**.[7] Similarly, hydrogen analog **3a** is reasonably converted to **4a** and **10** as depicted in Scheme 1, while **1b** would be first converted to (η^3-silapropenyl)-(trimethylsilyl)tricarbonylruthenium (**5b**) as shown in Scheme 2. However, in the case of **5b**, the trimethylsilyl group on the ruthenium would not move to the C(2) atom due to the steric hindrance caused by the phenyl group at the position 2. The reaction paths leading to **1a** and **2a** are not clarified yet at this moment.[11] However, in the case of hydrogen analogue **3b**-(***d***), the hydrogen (deuterium) atom on the ruthenium which is smaller than the silyl group would be able to migrate to the C(2) atom to give ruthenacycle **11b**. Ruthenacycle **11b** undergoes retro-cycloadditon to afford **4b**-(***d***) and silylene complex **10**. Although the detailed mechanism of the silylene extrusion reaction is not fully established, silapropenyl and silylene ruthenium complexes are suggested as key intermediates.

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